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(54) METHOD FOR MANUFACTURING CHLOROPRENE POLYMER AND COMPOSITION THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new method for manufacturing a chloroprene polymer that controls the latex particle size, and enhances the polymerization rate so that the method is stable and gives excellent productivity.

SOLUTION: A chloroprene polymer with a small latex particle size is manufactured at a high polymerization velocity, by radically polymerizing a monomer mixture comprising 2-chloro-1,3-butadiene in the presence of ≥ 0.1 and <10 parts by mass of an alcohol per 100 parts by mass of the total monomers. It is particularly preferable that the alcohol is substantially insoluble in water, having a solubility in water at 20° C of ≤ 1 g/100 g. It is further preferable that the alcohol is a saturated monohydric alcohol represented by the following formula (1) that can further enhance the polymerization rate.

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CLAIMS

[Claim(s)]

[Claim 1] In the bottom of 0.1 or more mass part existence of alcohols of less than ten mass part to a total of 100 mass parts of a monomer, A manufacturing method of a chloroprene polymer carrying out the radical polymerization of the monomeric mixture containing a 2-chloro-1,3-butadiene independent or 2-chloro-1,3-butadiene.

[Claim 2] A manufacturing method of the chloroprene polymer according to claim 1 with which mean particle diameter of latex is characterized by not less than 20-nm being less than 150 nm.

[Claim 3] A manufacturing method of a chloroprene polymer of claim 1-2 given in any 1 paragraph in which a diameter of grain of maximum size of latex is characterized by not less than 50-nm being less than 300 nm.

[Claim 4] A manufacturing method of a chloroprene polymer of claim 1-3 given in any 1 paragraph, wherein emulsifiers are rosin acids.

[Claim 5] A manufacturing method of a chloroprene polymer of claim 1-4 given in any 1 paragraph for which alcohols are characterized by being [whose solubility to water at 20 ** is 1g/100 g or less] alcohols insoluble to water substantially.

[Claim 6] A manufacturing method of a chloroprene polymer of claim 1-5 given in any 1 paragraph, wherein alcohols are saturation monohydric alcohol of the carbon numbers 3-20 expressed with a lower type.

[Formula 1]

C_nH_{2n+1}OH (炭素数nは整数で、3≤n≤20) 化学式 (1)

[Claim 7] A manufacturing method of a chloroprene polymer of claim 1-6 given in any 1 paragraph, wherein a chloroprene polymer is a sulfur denaturation chloroprene polymer.

[Claim 8] A chloroprene polymer constituent of claim 1-7 given in any 1 paragraph.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of a chloroprene polymer.

It is related with the art of control of a rate of polymerization, control of the diameter of a latex particle, and the stability of latex.

[0002]

[Description of the Prior Art] In radical polymerizations, such as monomers other than the former and 2-chloro-1,3-butadiene, for example, styrene, acrylic ester, and methacrylic acid ester, Many ** are just studied and reported to the art which adds alcohols from the purpose of control of the diameter of a latex particle, and the improvement in a rate of polymerization. In "Journal of Polymer Science : Part A : In Polymer Chemistry, Vol.39, No.6-2001, and page.898-912." Sodium persulfate was used as an initiator, sodium dodecylbenzenesulfonate was used as an emulsifier, and the radical emulsion polymerization of styrene is reported under three kinds of existence of alcohols (1-butanol, 1-pentanol, 1-hexanol). In "Polymeric Materials Science and Engineering, Vol.80, 1999, and page.554-555." As a redox system initiator, ammonium persulfate N,N,N',N'-tetramethylethylenediamine, The radical emulsion polymerization of butyl acrylate, ethyl acrylate, butyl methacrylate, ethyl methacrylate, methyl methacrylate, and styrene is reported under existence of 1-pentanol, using sodium dodecylbenzenesulfonate as an emulsifier. In "Journal of Applied Polymer Science, Vol.68, No.12, 1998, and page.2029-2039." Ammonium persulfate sodium hydrogen sulfite was used as a redox system initiator, sodium dodecylbenzenesulfonate was used as an emulsifier, and the radical emulsion polymerization of butyl acrylate and styrene is reported under existence of cetyl alcohol (namely, 1-hexadecanol). In "Polymer, Vol.37, No.12, 1996, and page.2509-2516." Cumene hydroperoxide ferrous sulfate was used as a redox system initiator, sodium lauryl sulfate was used as an emulsifier, and the radical emulsion polymerization of styrene is reported under existence of cetyl alcohol (namely, 1-hexadecanol).

[0003] In the radical polymerization of 2-chloro-1,3-butadiene, the example which uses alcohols for the purpose of control of the diameter of a latex particle and the improvement in a rate of polymerization is not found. About addition of the alcohols at the time of the radical polymerization of 2-chloro-1,3-butadiene, Suspension or the art which carries out an emulsion polymerization is proposed under existence of the alcohols to which miscibility with water is indicated to be polyvinyl alcohol for a butadiene series monomer as a stabilization solvent in a JP,6-145426,A gazette (applicant: load corporation). The art indicated in this gazette aims at improvement of the film formation characteristics of latex and adhesives, and is not connected with control of the diameter of a latex particle, and/or a rate of polymerization made into the technical problem by this invention. Although the suitable addition of alcohols is made into ten and to 100 mass part to monomer 100 mass part in this gazette, now, there are too many additions and it is the art which has a problem in the present when volatile organic solvent reduction is demanded.

[0004]

[Problem(s) to be Solved by the Invention] This invention controls the diameter of a latex

particle, and raises a rate of polymerization, it is stable and an object of this invention is to provide the new polymerization method of the chloroprene polymer excellent in productivity. [0005]

[Means for Solving the Problem] In the bottom of 0.1 or more mass part existence of alcohols of less than ten mass part to a total of 100 mass parts of a monomer which contains 2-chloro-1,3-butadiene as a result of repeating examination that this invention persons should attain the above-mentioned purpose. By carrying out the radical polymerization of the monomeric mixture containing 2-chloro-1,3-butadiene, a manufacturing method of a chloroprene polymer whose rate of polymerization it is small in a diameter of a latex particle, and is quick was invented.

[0006] Hereafter, the contents of this invention are explained in detail. Monomers in this invention are two or more monomeric mixtures which contain 2-chloro-1,3-butadiene independence or 2-chloro-1,3-butadiene as an essential monomer. As 2-chloro-1,3-butadiene and a copolymerizable monomer. For example, 2,3-dichloro-1,3-butadiene, 1-chloro-1,3-butadiene, 1,3-butadiene, 2-methyl-1,3-butadiene (namely, isoprene); styrene, acrylonitrile, acrylic acid, acrylic ester, methacrylic acid, and methacrylic acid ester are mentioned. And two or more kind copolymerization of these may be carried out.

[0007] A chloroprene polymer of this invention also contains a sulfur denaturation chloroprene polymer. To a total of 100 mass parts of a monomer containing 2-chloro-1,3-butadiene, 0.2-2 mass-part addition of the sulfur can be carried out, and a sulfur denaturation chloroprene polymer excellent in tensile strength, bending-fatigue-resistance nature, abrasion resistance, and a dynamic trait can be obtained by starting a radical polymerization reaction. It is known that a rate of polymerization of a system to which sulfur itself acts to delay a rate of polymerization, and sulfur originally exists in it will become slower than a system in which sulfur does not exist. In the system of reaction in which sulfur exists, especially, remarkable validity is shown and this invention can gather a rate of polymerization efficiently.

[0008] In particular an emulsifier and/or a dispersing agent that are used for an emulsion polymerization of this invention are not limited, and can use the various anionic form and Nonion type and a cation form emulsifier by which normal use is carried out to an emulsion polymerization. There are a carboxylic type, a sulfate ester type, etc. as an emulsifier of an anionic form. For example, alkyl sulfonate, alkyl aryl sulfate and sodium naphthalenesulfonic acid alkali metal salt of rosin acid and rosin acid and whose carbon number are 8-20 pieces, a condensate of formaldehyde, etc. are mentioned. As an Nonion type example, polyvinyl alcohol, polyvinyl ether, or its copolymer. A thing which carried out chemical modification of (for example, a copolymer with maleic acid), a polyvinyl pyrrolidone, its copolymer (for example, copolymer with vinyl acetate), or these (***) polymers, or a cellulose type derivative (hydroxyethyl cellulose) can be mentioned. Here, although a saponification degree of polyvinyl alcohol and a degree of polymerization in particular are not limited, a thing of 200-700 is preferred for 60-95-mol % and a degree of polymerization for a saponification degree. Polyvinyl alcohol said here may be a denaturation type (for example, a copolymer with acrylamide, an acetoacetylated type, a type which has a polyethylene unit (usually called RS type)). As an example of a cation form, there are alkylamine salt, aliphatic series quaternary ammonium salt, etc., for example, octadecyl trimethylammonium chloride, dodecyl trimethylammonium chloride, dilauryl dimethylammonium chloride, etc. are mentioned.

[0009] As an emulsifier used for this invention, alkali metal salt of rosin acids which are excellent in the stability of an emulsified state under polymerization is the most preferred. Rosin acids are non-volatile resin (common-name rosin) of rosin, and here in detail, It is a mixture of tricyclic resin acid, such as abietic acid, neabietic acid, parous thorin acid, REBOPIMARU acid, dehydroabietic acid, pimaric acid, isopimaric acid, SANDARAKO pimaric acid, KOMUN acid, anti Copal acid, run bell triane acid, dihydroAGATO acid, and acetyliso KYUPURESHIN acid. Composition ratio of these tricyclic resin acid changes with a raw material (material wood), an origin, a processing method, etc., and is not restricted in particular. A thing more than 30 mass % is easy to come to hand industrially, and especially abietic acid has it. [preferred]

[0010] An addition of an emulsifier in this invention and/or a dispersing agent has 0.2 to 10 preferred mass part to a total of 100 mass parts of an initial preparation monomer. In the case of less than 0.2 mass parts, emulsification power is not enough, and if ten mass parts are

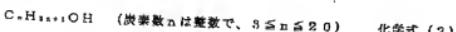
exceeded, it may have an adverse effect on the physical properties of rubber finished from latex.

[0011] Hydroxyl replaces a hydrogen atom of hydrocarbon of a chain or alicyclic with alcohols in this invention. A position of the number of hydroxyls of intramolecular and hydroxyl of intramolecular is not limited. Lower alcohol (five or less carbon number) and higher alcohol (six or more carbon numbers) may be sufficient, and it may have an unsaturated bond in intramolecular.

[0012] In particular, if solubility to water at 20 ** is saturated monohydric alcohol which is 1g/100 g or less and which is preferred in water as for insoluble alcohols, and is substantially expressed further with a lower type (2), alcohols can raise a rate of polymerization further and are preferred.

[0013]

[Formula 2]



[0014] As alcohols expressed with an upper type (2), Specifically 1-propanol (n= 3), 2-propanol (n= 3), 1-butanol (n= 4), 1-pentanol (n= 5), 1-hexanol (n= 6), 1-heptanol (n= 7), 2-heptanol (n= 7), 3-heptanol (n= 7), 4-heptanol (n= 7), 1-octanol (n= 8), 2-octanol (n= 8), 1-nonanol (n= 9), 2-nonanol (n= 9), 1-decanol (n= 10), 1-undecanol (n= 11), 1-dodecanol (namely, lauryl alcohol, n= 12), 1-hexadecanol (namely, cetyl alcohol, n= 16), stearyl alcohol (n= 18), etc. are mentioned.

[0015] An addition of alcohols is less than ten mass part 0.1 or more mass part to a total of 100 mass parts of a monomer containing 2-chloro-1,3-butadiene. If it is this range, the best effect will be acquired to a rate of polymerization.

[0016] Preparation conditions in particular, such as how to teach the pH of emulsified liquid required in order to advance an emulsion polymerization stably and safely, a charge of water, and a monomer, are not limited. What is necessary is just to choose appropriately according to a kind of a monomer and/or emulsifier.

[0017] Quantity of water is 90 to 150 mass part preferably 80 to 250 mass part to a total of 100 mass parts of a monomer. In less than 80 mass parts, it becomes easy to condense a latex particle. If 250 mass parts are exceeded, solid content of latex becomes low, as a result latex will be condensed or productivity will worsen at a process of making solids (a sheet, a pellet, a chip, etc.) to a polymer in latex by freezing, desiccation, etc.

[0018] Potassium persulfate, benzoyl peroxide, ammonium persulfate and hydrogen peroxide which are used by the usual radical polymerization as a polymerization initiator, t-butyl hydroperoxide, etc. are used. It may be the redox system initiator combined with a reducing agent.

[0019] Although a kind in particular of chain transfer agent of a chloroprene polymer in this invention is not limited and can use what is usually used for an emulsion polymerization of 2-chloro-1,3-butadiene. For example, long chain alkyl mercaptan, such as n-dodecyl mercaptan and tert-dodecyl mercaptan. Publicly known chain transfer agents, such as dialkyl xantho gene disulfide, such as diisopropyl xantho gene disulfide and diethyl xantho gene disulfide, and iodoform, can be used.

[0020] Conversion is performed in the range of 50 to 100% of an inversion rate from a practical viewpoint, subsequently adds polymerization inhibitor and makes it stop. 2,6-tertiary-butyl 4-methyl phenol, phenothiazin, hydroxylamine, etc. can be used for a terminator (polymerization inhibitor) of a polymer, for example. In order to perform a stable polymerization, 0-100 ** of polymerization temperature is preferred, and it is 0-55 ** more preferably.

[0021] As for latex mean particle diameter in this invention, it is preferred that D50% particle diameter (particle diameter from which accumulation particle distribution by a volume reference will be 50% = it is also called a median diameter or a median diameter) by a laser-diffraction-and-scattering method (it is also called laser diffractometry) is not less than 20 nm less than 150 nm. When mean particle diameter is less than 20 nm or not less than 150 nm, the emulsion stability of latex may worsen. In order to speed up a rate of polymerization furthermore, it is preferred that an overall diameter of latex is not less than 50 nm less than 300 nm. When a diameter of grain of maximum size is less than 50 nm or not less than 300 nm, the emulsion

stability of latex may worsen.

[0022] With a laser-diffraction-and-scattering method, apply a laser beam to particles distributed in carrier fluid, and it uses that an intensity pattern of diffraction/scattered light of a laser beam is dependent on a size of particles. It is the method of observing these and searching for particle size distribution using the Fraunhofer (Fraunhofer) diffraction theory and an I (Mie) scattering theory. As commercial measuring equipment, SALD-2000 (made by Shimadzu Corp.), LA-910W (made by Horiba, Ltd.), LA-920 (made by Horiba, Ltd.), Coal tar LS (made by coal tar incorporated company), a coal tar N4 plus type submicron particle analyzer (made by coal tar incorporated company), Microtrac UPA (made by Nikkiso Co., Ltd.), etc. are mentioned.

[0023] quantity of an unreacted monomer contained in sample latex in a measurement time — not related — decompression under a polymerization reaction and after a polymerization reaction stop — which latex after warming etc. remove a monomer may be sufficient.

[0024] A use in particular of a chloroprene polymer manufactured by this invention is not limited. It is the same as a use of the conventional chloroprene polymer. A solid can be made to latex of a chloroprene polymer of this invention if a polymer is isolated and dried [rinse and] by freezing coagulation, curing salting, etc. This is processible into various materials for agriculture and industry with publicly known vulcanization and foaming (a closed cell, an open cell), or forming technique, and also it can use for solvent system adhesives, a solvent system paint, a solvent system binder, etc. by making it dissolve in a suitable organic solvent. By what a tackifier, a plasticizer, a thickener, a hardening agent (vulcanizing agent), a rubber accelerator, etc. are blended with latex of a chloroprene polymer for if needed, for example. Drainage system adhesives, resorcinol formaldehyde latex adhesive (RFL adhesives), A drainage system paint, a flattening, a coating agent (coating), a finishing agent, a liquid-applied-membrane-waterproofing agent, A binder for molding powdered substances, such as a rubber chip, sand, and various pulverized powders (binder), Immersion products, such as a processing agent (binder) of textiles, such as carpet processing, or a textile, a glove, and a contraceptive, It can be used for latex for vegetation for fixing a seed, manure, and the ground to a water-proofing agent, sediment discharge prevention (earth-and-sand preventing scattering) latex, a ground surface, and a mat of footwear, a concrete modifier, an asphalt modifier, etc.

[0025]

[Example] Hereafter, although an example explains this invention, these examples do not limit this invention.

[0026] [Example 1] Rosin acid sodium (made by HARIMA CHEMICALS, Inc.) was dissolved by 3.5 mass parts, 1.0 mass parts were dissolved [sodium hydroxide] for the condensate of 0.3 mass parts, sodium naphthalenesulfonate, and formaldehyde in distilled water 130 mass part at 40 **, and rosin acid chloride solution was produced. Sulfur 0.5 mass part and cetyl alcohol (1-hexadecanol) 2 mass part were dissolved in 2-chloro-1,3-butadiene 100 mass part, and the monomer solution was produced. Rosin acid chloride solution and a monomer solution are prepared, holding at 35 **, it agitated for 10 minutes and the reactor with a content volume of 5 l. was made to emulsify in a nitrogen atmosphere. Then, it applied for 30 minutes and temperature up was carried out to 40 **, as a polymerization initiator, the 2 mass % solution of potassium persulfate was dropped at the rate of per minute 0.015 mass parts (wet), and the polymerization reaction was started in the place in which solution temperature was stabilized at 40 **. When inversion rate 70 mass % was reached, the emulsion containing a chloroprene monomer, distilled water, thiophenylamine, and diethylhydroxylamine was added, and the polymerization was terminated. The rate of polymerization and the diameter of a latex particle were measured by the following method.

[0027] [Rate-of-polymerization calculation] After starting dropping of the polymerization initiator, the specific gravity (rho) of 0 hour, 0.5 hour, 1.0 hour, and 1.5 hours after was measured. Based on the data, change (delta rho/hr) of the specific gravity per hour was calculated with the least square method.

[0028] [Particle diameter measurement] Dilution adjustment of the latex immediately after terminating a polymerization reaction was carried out with distilled water so that solids concentration might become 0.05 mass %, and mean particle diameter and the diameter of grain

of maximum size were measured by Microtrac UPA (made by Nikkiso Co., Ltd.).
 [0029][Example 2] It polymerized by the same method as Example 1 except [all] having transposed cetyl alcohol 2 mass part of Example 1 to 1-hexanol 0.8 mass part. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1.
 [0030][Example 3] It polymerized by the same method as Example 1 except [all] having transposed cetyl alcohol 2 mass part of Example 1 to 1-pentanol 0.7 mass part. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1.
 [0031][Example 4] It polymerized by the same method as Example 1 except [all] having transposed cetyl alcohol 2 mass part of Example 1 to 1-propanol 0.5 mass part. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1.
 [0032][Comparative example 1] It polymerized by the same method as Example 1 except [all] not adding alcohols to a monomer solution. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1.
 [0033]The evaluation result from which Examples 1-4 and the comparative example 1 were acquired was shown in Table 1.

[Table 1]

モノマー溶液 [質量部]	実験例				比較例 1
	1	2	3	4	
2-メト-1,3-ブチジエン 2-メト-1,3-ブチジン	—	—	—	—	—
硫黄	1.00	1.00	1.00	1.00	1.00
カーボンディシルメルカプタン	0.5	0.5	0.5	0.5	0.5
セチルアルコール	—	—	—	—	—
1-ヘキサノール	2	—	—	—	—
1-ペンタノール	—	0.8	—	—	—
1-ブロバンノール	—	—	0.7	—	—
ロジン酸水素被 [質量部]					
無留水	1.30	1.30	1.30	1.30	1.30
ロジン酸ナトリウム	3.5	3.5	3.5	3.5	3.5
水酸化ナトリウム	0.3	0.3	0.3	0.3	0.3
ナフタレンスルホン酸ナトリウムと KATAKATととの組合物	1.0	1.0	1.0	1.0	1.0
過酸化水素ナトリウム	—	—	—	—	—
重合条件					
重合温度 [℃]	40	40	40	40	40
重合速度測定結果					
$\Delta \rho / h^{-1}$	0.032	0.028	0.020	0.020	0.017
粒子径測定結果					
平均粒子径 [nm]	118	121	128	125	162
最大粒子径 [nm]	200	204	289	243	310

注) $\Delta \rho / h^{-1}$ は時間当たりの比重 (ρ) の変化

[0035][Example 5] Rosin acid sodium (made by HARIMA CHEMICALS, Inc.) to distilled water 130 mass part 3.5 mass parts, 1.0 mass parts and sodium-hydrogen-sulfite 0.5 mass part were dissolved [sodium hydroxide] for the condensate of 0.3 mass parts, sodium naphthalenesulfonate, and formaldehyde at 40 **, and rosin acid chloride solution was produced. 2-chloro-1,3-butadiene 100 mass part, n-dodecyl mercaptan 0.15 mass part, and cetyl alcohol (1-hexadecanol) 2 mass part were dissolved, and the monomer solution was produced. Rosin acid chloride solution and a monomer solution are prepared, holding at 10 **, it agitated for 10 minutes and the reactor with a content volume of 5 l. was made to emulsify in a nitrogen atmosphere. In the state of 10 ** of solution temperature, as a polymerization initiator, the 2 mass % solution of potassium persulfate was dropped at the rate of per minute 0.015 mass parts (wet), and the polymerization reaction was started. When inversion rate 60 mass % was reached, the emulsion containing a chloroprene monomer, distilled water, thiophenylamine, and diethylhydroxylamine was added, and the polymerization was terminated. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1.

[0036][Example 6] It polymerized by the same method as Example 5 except [all] having transposed cetyl alcohol 2 mass part of Example 5 to 1-hexanol 0.8 mass part. The measuring

method of a rate of polymerization and particle diameter is the same as that of Example 1. [0037][Example 7] It polymerized by the same method as Example 5 except [all] having transposed cetyl alcohol 2 mass part of Example 5 to 1-pentanol 0.7 mass part. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1. [0038][Example 8] It polymerized by the same method as Example 5 except [all] having transposed cetyl alcohol 2 mass part of Example 5 to 1-propanol 0.5 mass part. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1. [0039][Comparative example 2] It polymerized by the same method as Example 5 except [all] not adding alcohols to a monomer solution. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1. [0040] The evaluation result from which Examples 5-8 and the comparative example 2 were acquired was shown in Table 2.

[0041]

[Table 2]

モノマー-溶媒 〔質量部〕	共通例				比較例 2
	5	6	7	8	
2-エト-1,3-ブチエン	-	-	-	-	-
2-エト-1,3-ブチエン	1.00	1.00	1.00	1.00	1.00
硫酸	-	-	-	-	-
n-ドデシルメルカプタン	0.15	0.15	0.15	0.15	0.15
セテルアルコール	2	-	-	-	-
1-ヘキサンオール	-	0.8	-	-	-
1-ベンゼンオール	-	-	0.7	-	-
1-ブロボノール	-	-	-	0.5	-
ロジン酸塩水溶液 〔質量部〕					
蒸留水	1.30	1.30	1.30	1.30	1.30
ロジン酸ナトリウム	3.5	3.5	3.5	3.5	3.5
水酸化ナトリウム	0.3	0.3	0.3	0.3	0.3
ナフタレンスルホ酸ナトリウムと ホルムアルデヒドとの複合物	1.0	1.0	1.0	1.0	1.0
重複酸水素ナトリウム	0.5	0.5	0.5	0.5	0.5
重合条件					
基準温度 [℃]	10	10	10	10	10
重合速度測定結果					
$\Delta p / h r$	0.028	0.025	0.025	0.025	0.022
粒子径測定結果					
平均粒子径 [nm]	1.88	1.43	1.47	1.40	1.54
最大粒子径 [nm]	2.62	2.77	2.80	2.69	3.05
△p / h r … 1時間当たりの比重 (p) の変化					

[0042][Example 9] Rosin acid sodium (made by HARIMA CHEMICALS, Inc.) to distilled water 130 mass part 3.5 mass parts, 1.0 mass parts and sodium-hydrogen-sulfite 0.5 mass part were dissolved [sodium hydroxide] for the condensate of 0.3 mass parts, sodium naphthalenesulfonate, and formaldehyde at 40 **, and rosin acid chloride solution was produced. n-dodecyl mercaptan 0.2 mass part and cetyl alcohol (1-hexadecanol) 2 mass part were dissolved in 2-chloro-1,3-butadiene 80 mass part and 2-methyl-1,3-butadiene 20 mass part, and the monomer solution was produced. Rosin acid chloride solution and a monomer solution are prepared, holding at 30 **, it agitated for 10 minutes and the reactor with a content volume of 5 l. was made to emulsify in a nitrogen atmosphere. Then, it applied for 20 minutes and temperature up was carried out to 35 **, as a polymerization initiator, the 2 mass % solution of potassium persulfate was dropped at the rate of per minute 0.015 mass parts (wet), and the polymerization reaction was started in the place in which solution temperature was stabilized at 35 **. When inversion rate 60 mass % was reached, the emulsion containing a chloroprene monomer, distilled water, thiadiphenylamine, and diethylhydroxylamine was added, and the polymerization was terminated. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1.

[0043][Example 10] It polymerized by the same method as Example 9 except [all] having transposed cetyl alcohol 2 mass part of Example 9 to 1-hexanol 0.8 mass part. The measuring

method of a rate of polymerization and particle diameter is the same as that of Example 1. [0044][Example 11] It polymerized by the same method as Example 9 except [all] having transposed cetyl alcohol 2 mass part of Example 9 to 1-pentanol 0.7 mass part. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1. [0045][Example 12] It polymerized by the same method as Example 9 except [all] having transposed cetyl alcohol 2 mass part of Example 9 to 1-propanol 0.5 mass part. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1. [0046][Comparative example 3] It polymerized by the same method as Example 9 except [all] not adding alcohols to a monomer solution. The measuring method of a rate of polymerization and particle diameter is the same as that of Example 1. [0047] The evaluation result from which Examples 9-12 and the comparative example 3 were acquired was shown in Table 3.

[0048]

[Table 3]

モノマー溶液 〔質量部〕	実施例				比較例 3
	9	10	11	12	
2-ブタノ-1,3-ジ-7-オクエン	2.0	2.0	2.0	2.0	2.0
2-ブタノ-1,3-ジ-9-オクエン	8.0	8.0	8.0	8.0	8.0
硫酸	-	-	-	-	-
ヒドロデシルメルカプタン	0.20	0.20	0.20	0.20	0.20
セチルアルコール	2	-	-	-	-
1-ヘキサンオール	-	0.8	-	-	-
1-ペントノール	-	-	0.7	-	-
1-ブロノノール	-	-	-	0.5	-
ロジン酸塩水溶液 〔質量部〕					
蒸留水	1.30	1.30	1.30	1.30	1.30
ロジン酸ナトリウム	3.5	3.5	3.5	3.5	3.5
水酸化ナトリウム	0.3	0.3	0.3	0.3	0.3
ナフタレンスルホ酸ナトリウムと ホムテラヒドロキサンとの混合物	1.0	1.0	1.0	1.0	1.0
重碳酸水素ナトリウム	0.5	0.5	0.5	0.5	0.5
重合条件					
重合温度 [℃]	3.5	3.5	3.5	3.5	3.5
重合速度測定結果 $\Delta \rho / h$	0.030	0.031	0.029	0.028	0.025
粒子径測定結果 平均粒子径 [nm]	14.5	14.5	14.1	14.2	15.1
最大粒子径 [nm]	26.4	26.1	28.0	25.8	31.8

(注) $\Delta \rho / h$: 1時間当たりの比重 (ρ) の変化

[0049]

[Effect of the Invention] In the point that a rate of polymerization is quick, and the point which can control mean particle diameter small, the manufacturing method (examples 1-12) of the chloroprene polymer of this invention is superior to the conventional manufacturing method (comparative examples 1-3) so that more clearly than Tables 1-3.

[Translation done.]